

QUANTIFYING FLUIDITY DEVELOPMENT AND MOBILITY IN COALS BY IN-SITU ^1H NMR

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ABSTRACT

After briefly reviewing the information that has been obtained to date using ^1H NMR to rationalise various phenomena associated with fluidity development, the improvements that can be achieved with various additives for poor coking coals will be described from both a practical and a fundamental standpoint. Trapping neutral oils from coal tar within briquettes prepared with phenolic binders enhances the mobility of the semi-fluid material for poor coking coal without significantly increasing the concentration. In terms of polymer additives, polyurethanes are unique in having a fluidity range that overlaps those of coals. Again, their addition vastly enhances the mobility of the semi-fluid material generated from poor coking coals but, unlike pitches, they do not dissolve any additional coal due to the high volatile losses. However, flexible foams have the ability to act as a plasticiser for much of the macromolecular structure in bituminous coals at relatively low temperatures (200-300°C). For high volatile coking coals, the addition of a petroleum coker feed (vacuum resid) can virtually render them completely fluid which accounts for the high yield of mesophase obtained in the resultant semi-cokes.

INTRODUCTION

In-situ broadline ^1H NMR has proved to be a highly successful technique for investigating the molecular motion in coals and pitches during carbonisation⁽¹⁻¹³⁾. There are usually two contributions to free induction decays of coals arising from mobile (faster relaxing) and rigid (slower relaxing) components that display Lorentzian and Gaussian decays, respectively. Coal, as a cross-linked macromolecular network, gives rise to a substantial inert component that does not soften and this produces a broad Gaussian peak in the NMR spectrum with a much narrower Lorentzian peak from the mobile material superimposed. The peak width is inversely proportional to the spin-spin relaxation time (T_2) of the fluid phase and is highly responsive to changes in mobility and this behaviour can be monitored as a function of temperature. It is fitting to describe recent work at the University of Strathclyde on the use of in-situ ^1H NMR to quantify phenomena associated with fluidity development in carbonisation on two counts. Firstly, Professor Sanada's own pioneering contribution to the development of in-situ ^1H NMR which dates back to the late 1970s⁽¹⁾. Secondly, fluidity development is inexorably linked to the thermal breakdown of the network structures existing in bituminous coals. After summarising the information that has been obtained to date using ^1H NMR to rationalise various phenomena associated with fluidity development, the improvements that can be achieved with additives in the behaviour of poor coking coals will be described from both a practical and a fundamental standpoint.

OVERVIEW OF EARLIER WORK

After the technique was first used by Sanada in the late 70s⁽¹⁾ to identify fluid material from coal and pitch at the early stages of carbonisation, Lynch, Sakurovs and co-workers, from the early 80s onwards⁽³⁻⁹⁾, detected both the rigid and fluid phases using a bench top spectrometer and have referred to their approach as Proton Magnetic Resonance Thermal Analysis (PMRTA). They have used mainly the empirical parameter, M_{2T16} , corresponding to the second moment integration limited at a width of 16 kHz, for gauging the reductions in fluidity as a function of oxidation and solvent extraction and the increases due to pitch/model compound addition. Of particular note is the quantification of interactive effects between different components in blends with both pitch and decacyclene being found to have a much greater effect than predicted on improving fluidity⁽⁷⁾. More recently, the issue of synergism between coals in coking blends has been addressed by Sakurovs⁽⁹⁾. In the majority of the binary coal blends investigated, both positive and negative interactions in terms of fluidity enhancement occurred. Positive interactions were generally greatest for blends of high and low volatile bituminous coals while semi-anthracite merely acted as a diluent to suppress fluidity.

Using both the amount and the T_2 of the mobile hydrogen, work at Strathclyde has established that, at maximum fluidity, the mobile phase accounts for 35-50% of the hydrogen remaining for good coking coals with both its concentration and mobility increasing up to this temperature, T_{2s} at maximum fluidity being *ca.* 100 μ s. In contrast, coals that exhibit no softening in the Gieseler generate *ca.* 20% semi-fluid hydrogen with a T_2 of 60-70 μ s⁽¹⁰⁾. Like PMRTA⁽⁶⁾, measurements at Strathclyde have established that some high volatile bituminous coals that display little plasticity development in the Gieseler can generate appreciable fluidity, probably due to volatiles (potential metaplast) escaping at lower temperatures in the Gieseler. Reducing the particle size below *ca.* 150 μ m suppresses plasticity through a reduction in the mobility of the fluid phase with the concentration of rigid material remaining constant. This effect was considerably more pronounced with slow than fast heating (3-4 *cf.* 30°C min⁻¹). In contrast, suppressing the fluidity by mild oxidation reduced primarily the concentration of the fluid phase. Isothermal treatments gave rise to a loss of fluidity due to reductions in both the proportion and mobility of the fluid component. However, the in-situ measurements have confirmed that plasticity development is a reversible phenomenon provided that relatively fast quenching rates (*ca.* 75°C min⁻¹) are used.

As early as 1860, de Marsilly showed that removing solvent extractable material destroys the fluid properties of coking coals⁽¹⁴⁾ as later detected by standard methods, including Gieseler plastometry and dilatation^(15,16). However, it was not possible from standard tests to resolve quantitatively the contributions from the extractable material in coal and the metaplast generated thermally to the overall concentration of fluid material generated. High temperature ¹H NMR measurements were thus carried out on a suite of bituminous coals and their pyridine extracts and residues⁽¹¹⁾. Between one-third and a half of the mobile phase at maximum fluidity is metaplast for good coking coals. Further, taking the separate contributions from the pyridine extracts and residues, the predicted proportions and spin-spin relaxation times of the total hydrogen in the fluid phase at maximum fluidity were in close agreement with those observed for the whole coals. Thus, the pyridine-extractables do not appear to increase the amount of metaplast generated and serve mainly to increase the mobility of the fluid phase.

To help ascertain the contribution semifusinite makes to plasticity development during carbonisation, vitrinite and semifusinite concentrates with purities over 90% were separated by density gradient centrifugation from a medium volatile Australian bituminous coal⁽¹²⁾. For the vitrinite concentrates, the increases in reflectance and the degree of aromatic ring condensation with density correlate with the decreasing mobility of the fluid material. For the coal investigated, the overall contribution of the reactive semifusinite to the fluid phase at maximum fluidity is estimated to be 15 % (*ca.* 4 of the 30 % mobile hydrogen observed). Although interactions between maceral groups may take place in the original coal matrix, mixtures of the vitrinite and semifusinite concentrates did not reveal any synergism.

Hydrogen-donor ability has been ascribed as one of the factors responsible for the stabilisation of the plastic phase during coal carbonisation^(17,18) and to investigate this quantitatively, the interactions of a poor coking bituminous coal with a heat-treated coal tar pitch (CTP) and with a hydrogen-donor pitch (HDP, >450°C residue) obtained from a two-stage coal liquefaction process were compared⁽¹³⁾. When the CTP was added to the coal (25% w/w, 150-250 μ m), the amount of fluid material increased by nearly 20% more than that predicted at maximum fluidity. However, an even larger synergistic effect was observed with the HDP as a result of hydrogen transfer. By 400°C, 90% of the fluid phase concentration observed at 450°C had already been generated, corresponding to an enhancement of 50% over that predicted. However, particle size had a major impact with no enhancement in fluidity was detected below 45 μ m. Other possible approaches to the well-established use of coal tar pitch to enhance fluidity that have been investigated by in-situ ¹H NMR will now be described. The three avenues that have been investigated here are:

- (i) the use of polyurethanes since, in terms of common polymers, these are unique in having a fluidity range that overlaps those of coals;
- (ii) trapping coal tar within briquettes prepared with cold cure phenolic binders prepared from coal tar acids; and
- (iii) the use of a coker feed vacuum resid (VR) to prepare coke rich in mesophase.

EXPERIMENTAL

All the NMR measurements were conducted using a Bruker MSL100 spectrometer equipped with a ¹H high temperature Doty NMR probe, as previously described⁽¹⁰⁻¹³⁾. Approximately 50 mg of sample was packed lightly into a zirconia container and heated with an average heating rate of 4°C min⁻¹ from 25°C up to 550°C in a nitrogen atmosphere. Spectra were obtained at a number of different temperatures and transferred from the spectrometer to a PC for

Fourier transformation and the resultant spectra were fitted to a Lorentzian (narrower peak, fluid material) and a Gaussian (broader peak, rigid material) component.

For the experiments with polyurethane, a rigid and a flexible foam (20% w/w of the foams in the coal blends) were used in co-carbonisation tests with a poor coking coal (the same low volatile bituminous coal (designated AUS-4) as used in the earlier study with pitches⁽¹³⁾). Cold cure briquettes from a similar coal (designated CAN-1) were prepared with a phenolic resole prepared using the acids from low temperature coal tar as described elsewhere⁽¹⁹⁾. However, a resole was also prepared using the whole tar and this also cured successively, effectively trapping the neutral aromatics from the tar within the briquettes. High temperature ¹H NMR experiments were carried out on segments cut from the two types of briquettes and on a physical mixture of the coal with the tar acid resole (85:15 blend). A mass ratio of the VR to Powellton coal of 2:1 was used to replicate the published work of Schobert *et al.*⁽²⁰⁾ where coke with high mesophase content was prepared.

RESULTS AND DISCUSSION

Polyurethane co-carbonisation

Figure 1 shows the ¹H NMR spectra for the 80:20 blends of poor coking coal with the flexible and rigid foams at 450°C. Figures 2 and 3 present the variations with temperature in the proportion and T₂ of the mobile phase, respectively, for the poor coking coal and the blends of this coal with the flexible and rigid foams. The two foams differ in that methyldiisocyanate (MDI) moieties account for 35% of the carbon in the flexible foam compared to 75% in the rigid foam. Further, as well as isocyanate linkages, the rigid foam contains polyisocyanurate (PIR) moieties that confer considerable thermal stability. Thus, whilst the rigid foam is not liquefied fully to temperatures approaching 400°C by which time the volatile losses are high, the flexible foam is liquefied virtually completely by 200°C. This results in approximately 75% of the hydrogen being mobile (Figure 2) which corresponds approximately to 55% of the coal hydrogen, indicating a considerable plasticising effect by the aromatic diamines and diols that result from the cleavage of the isocyanate linkages. This is akin to the effect of polar solvents, such as pyridine, at ambient temperatures^(21,22), although the effect here is larger considering the non-swelling nature of the coal and the related low pyridine extraction yield⁽¹¹⁾. The T₂ of the flexible foam blend at ambient temperatures is high (*ca.* 250 μs, Figure 3) due to the highly flexible chains and it increases to over 500 μs due to the foam being liquefied as the urethane linkages are cleaved. Both the proportion and T₂ of the mobile phase decrease markedly as the flexible foam decomposes until 425°C when the metaplast is generated in significant quantities from the coal⁽¹¹⁾. For the rigid foam, the initial decrease in T₂ can be ascribed to the loss of water. However, as expected, the plasticising effect of the rigid foam is much less pronounced than that of the flexible foam with virtually all the mobile hydrogen below 350°C, which represents the onset of metaplast generation⁽¹¹⁾, being generated from the thermal decomposition of the foam.

By 450°C, the residue yields from both foams are small which means that virtually all of the fluid phase remaining is coal-derived. For this reason, the action of neither of the foams (within experimental error) results in an increase the proportion of mobile hydrogen close to maximum fluidity. However, the rigid foam in particular, for which the residue yield is greater than for the flexible foam, gives rise to a vast increase in T₂ of the mainly coal-derived fluid phase. Thus, the foam residue whilst displaying no appreciable solvent action in terms of increasing the proportion of mobile hydrogen, acts mainly to mobilise the semi-fluid phase to a much greater extent than found for the fluid phase in prime coals (*cf.* T₂ at 450°C of 200 μs for the blend with that of *ca.* 100 μs for good coking coals, albeit the latter contain much more mobile hydrogen). This action is essentially the same as that provided by the pyridine-solubles on the thermally generated metaplast (from the pyridine-insolubles) for good coking coals⁽¹¹⁾.

Coal tar addition to briquettes

It has been found that the enhanced fluidity obtained by trapping the neutral oils from low temperature tar within a cold cure briquette prepared in a laboratory press gives rise to a volumetric increase of 31% for the semi-coke briquette obtained at 600°C compared to only 9% for the normal tar acid resole formulation. Therefore, this initial study suggests that the resole made from whole coal oil can enhance the swelling properties of poor swelling coals considerably. Figures 4 and 5 show the variations with temperature in the proportion and T₂ of the mobile phase hydrogen, respectively, for the whole tar and normal tar acid resole cured briquettes, the green (non-cured) briquette for the whole tar resole and the coal itself. Although for the non-cured briquette, the neutral oils and constituents arising from the thermal decomposition of the binder give rise to an increase in the proportion and the T₂ of the mobile hydrogen at low temperatures, they volatilise below 350°C, resulting in little change in the fluidity characteristics between 400 and 500°C compared to the initial coal (Figures 4 and 5). Above 200-250°C once excess moisture have been removed, such increases in the proportion and

T_2 of the mobile hydrogen have largely been suppressed for the cured resin briquettes, suggesting that, in the case of the whole tar acid resole, the neutral oils have essentially been immobilised. However, for both the cured briquettes, there is an increase in T_2 for the fluid phase hydrogen from 60 to 80-120 μ s between 450 and 500°C (Figure 5), due to the later release of volatiles. The fact that the proportion of fluid hydrogen does not change appreciably indicates that most of the volatiles have been lost from the briquette section used for ^1H NMR and that, unlike CTP, the neutral oils and resin breakdown products are not liquefying the coal. Thus, the swelling action of these constituents in the cured briquettes can be attributed to their ability to mobilise the semi-fluid metaplast generated from the poor coking coal, much in the same way as the rigid polyurethane foam.

Vacuum resid liquefaction

Figure 6 shows the ^1H NMR spectrum obtained at 450°C from the blend of VR and Powellton coal. The rigid phase accounts for less than 4% of the total hydrogen and this proportion corresponds to over 80% of the coal hydrogen being liquefied. This observation, which represents the first full liquefaction experiment conducted by in-situ ^1H NMR, indicates that virtually all of the pre-asphaltenes (THF-insolubles, ca. 40% yield) obtained in the ex-situ liquefaction experiments⁽²⁰⁾ must soften in-situ. Above 450°C, the fluid phase forms semi-coke which, ex-situ, comprises high concentrations of mesophase that can be attributed to the extremely high fluidity observed here. However, unlike petroleum and coal tar pitch where two distinct mesophase types have been resolved with T_{2S} of ca. 20 and 70 μ s with the one having the longer disappearing as more mesophase is formed⁽²³⁾, only one solid phase with the shorter T_2 of 20 μ s is evident here for the VR/coal semi-coke. Thus, the intermediate phase considered to be attributable to gel-like material does not appear to form in significant proportions and the resulting signal is a composite from mesophase spheres and isotropic domains.

CONCLUSIONS

The description of the fluid phase in terms of the concentration and the T_2 of the mobile phase has enabled the effects of various additives during carbonisation to be rationalised in terms of whether they merely solvate the fluid phase as observed for the polyurethanes and the coal tar neutral aromatics within the briquette or, like the VR, dissolve additional coal.

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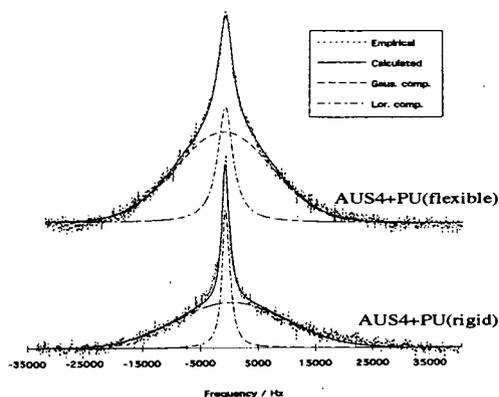


Figure 1 Comparison of ^1H NMR spectra for the blend of poor coking coal with flexible and rigid foams at 450°C

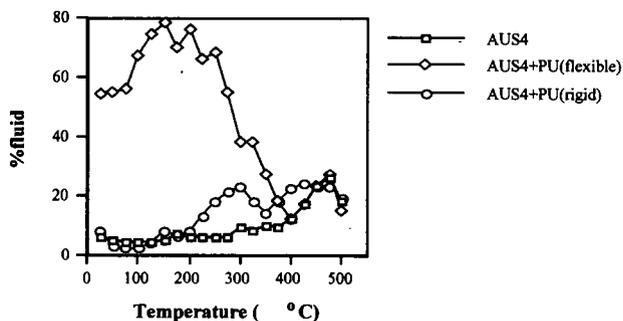


Figure 2 Variation with temperature in the proportion of the mobile phase hydrogen for the poor coking coal and the blends with the flexible and rigid foams (4:1)

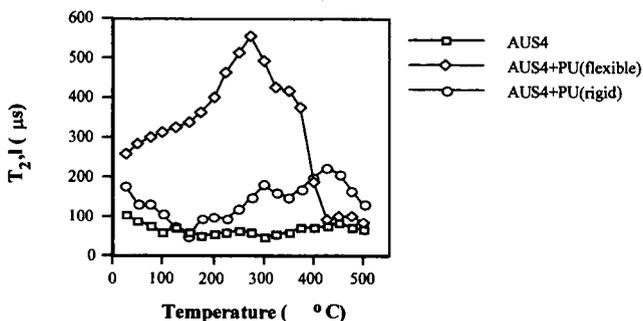


Figure 3 Variation with temperature in the T_2 of the mobile phase hydrogen for the poor coking coal and the blends with the flexible and rigid foams (4:1)

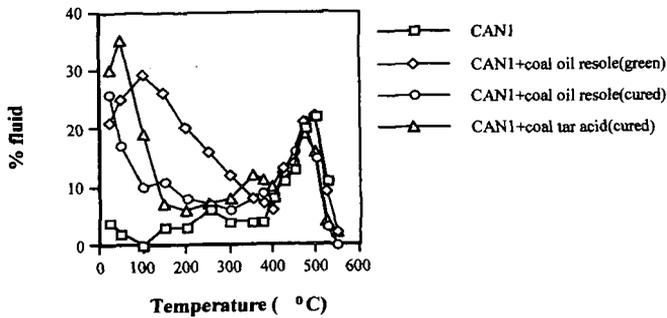


Figure 4 Variation with temperature in the proportion of the mobile phase hydrogen for the normal and neutral oil-containing cold cure briquettes and for the physical mixture of the coal (designated CAN 1) and low temperature coal tar

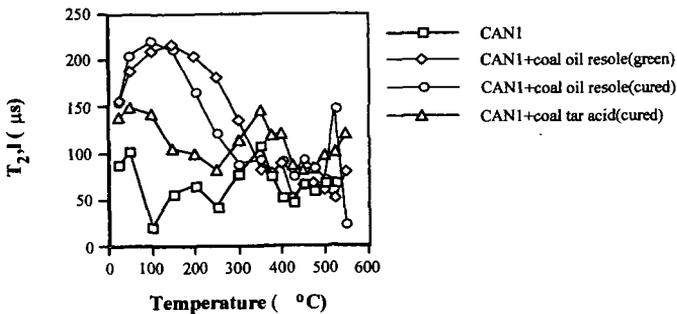


Figure 5 Variation with temperature in the T₂ of the mobile phase hydrogen for the normal and neutral oil-containing cold cure briquettes and for the physical mixture of the coal (designated CAN 1) and low temperature coal tar

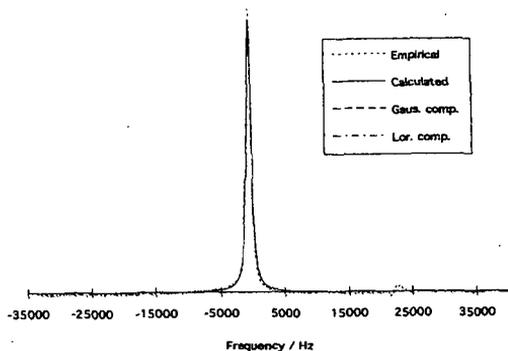


Figure 6 ¹H NMR spectrum obtained at 450°C for the blend of the vacuum resid and Powellton coal (2:1 w/w).